PROCEEDINGS

TECHNOLOGY TRANSFER CONFERENCE 1988
November 28 and 29, 1988
Royal York Hotel
Toronto, Ontario

SESSION D
ANALYTICAL METHODS

Sponsored by
Research and Technology Branch
Environment Ontario
Ontario, Canada

AASG

DP5

"AUTOMATED WATER SAMPLER FOR DIOXIN DETECTION AT PPQ LEVELS"
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The Ministry of the Environment is responsible for many
monitoring programs for organic contaminants. In particular,
there is a need to detect and quantify accurately the highly
toxic polychlorinated dibenzo-p-dioxins (PCDDs) and chlorinated
dibenzofurans (PCDFs) in the environment. Special attention is
directed at determining the exposure of the population to these
substances in drinking water. The current method of analysis for
these compounds in drinking water is by liquid-liquid extraction
of 10 L grab samples. The public demand for more information on
water quality requires lowering the detection limit to 1.0 ppq
while increasing the number of samples and maintaining high
standards of Quality Assurance--Quality Control.

The most effective way to meet these conflicting demands is
automated preconcentration at the test site. A safe, portable
sampling unit was required because existing liquid solvent
extractors cannot be used in a water treatment plant. One
example is the APLE unit which uses 8 L of solvent for a 200 L
batch of water. This unit was found to be too bulky and
cumbersome to fit the criteria of a portable sampling unit and,
the volume of solvent is not appropriate from a safety pint of
view. Other liquid-liquid extractors do not follow safety
restrictions since they involve discharge of dichloromethane.

In order to automate the preconcentration process the construction of an instrument was required in order to provide more acceptable collection techniques. Studies of liquid–solid extraction of organics from water shown that the technique could be used in a sampling unit. It is essential that in addition to the column, a filtering system be installed since raw and treated water which may contain particulate matter, could be analyzed. Two generations of automatic preconcentration samplers (APS) have been built in our laboratory to comply with the necessary criteria. The first prototype, Mark I APS, assisted in determining the important features for the Mark II, permitting the establishment of specific requirements for a safe, convenient analytical system.

The Mark II APS was designed to be rugged and portable for use at a wide variety of sampling sites. The preconcentration vessels (filters and columns) were made detachable so they may be returned to a central laboratory for analysis. Many safety features were incorporated to ensure safe use in a water treatment plant.

In the Mark II sampling unit a water reservoir was incorporated into which the raw or treated water sample is pumped. It provides a physical air break in the sample stream between the water and the sampler to prevent any black flow to the source. The sampler is also capable of providing a continuous injection and mixing of standards throughout the sampling period. A standard injection assembly consisting of a reservoir and precision pump can deliver the standard solution as a constant

proportion of the sample flow rate. This dynamic quality control of sampler performance during a sample run provides a valid reference for quantitation of the analyte as a function of time and matrix of the sample.

The preconcentration process in the sampler system provides a dual function; first to filter particulate from the sample stream and then to adsorb the remaining water soluble target compounds on the column for subsequent analysis. The filter system is based on setting the distinction between dissolved and insoluble particles at 0.45μm. The duplicate analytical systems each consist of 2 tubular filters placed in series to accommodate 50-100L of raw water. The adsorption technology in the present sampler utilizes XAD-2 resin for which sampling conditions and elution and detection procedures have been established to permit recovery and analysis of dioxins at the ppq level.

A schematic of water flow through the sampler is illustrated in figure 1. The overall design and placement of components are shown in figures 2 and 3. The water sample from a pressurized source enters through the "water in" port located at the back of the sampler into the water reservoir. The water is drawn through a mixing chamber, where the incoming water will be mixed with an internal standard, and is then split equally to provide duplicate samples. Each sample stream passes through a filter assembly, a high precision gear pump, an air release valve, and then a column. The air release valve is essential for removing air accumulated on the filter, preventing it from entering the column

and monitoring components. One sampling apparatus is located on each side of the sampler. The pumps are responsible for regulation of flow rate. The water flow and pressure of each sample stream is monitored by mechanical flow meters and pressure gauge to ensure identical sampling conditions. A pressure switch, located between the filter and column, is connected to a batch controller and can terminate a sample run if the pressure build-up from the columns occurs, or if low pressure due to cavitation from a blocked filter occurs. After passing through the columns, the two sampling streams join to pass the main electronic flow sensor which monitors the total water flow of the system. The flow sensor sends a signal to a digital flow meter and chart recorder for a readout and hard copy of the flow rate, and to the batch controller which records the total sample volume. A charcoal filter is placed prior to sample output to remove any residual organics. An analytical bypass controlled by three-way diverter valves diverts the water sample from the mixer to the charcoal filter. This feature flushes any residual water out of the reservoir and replaces it with a fresh water sample before initiating another sample run.
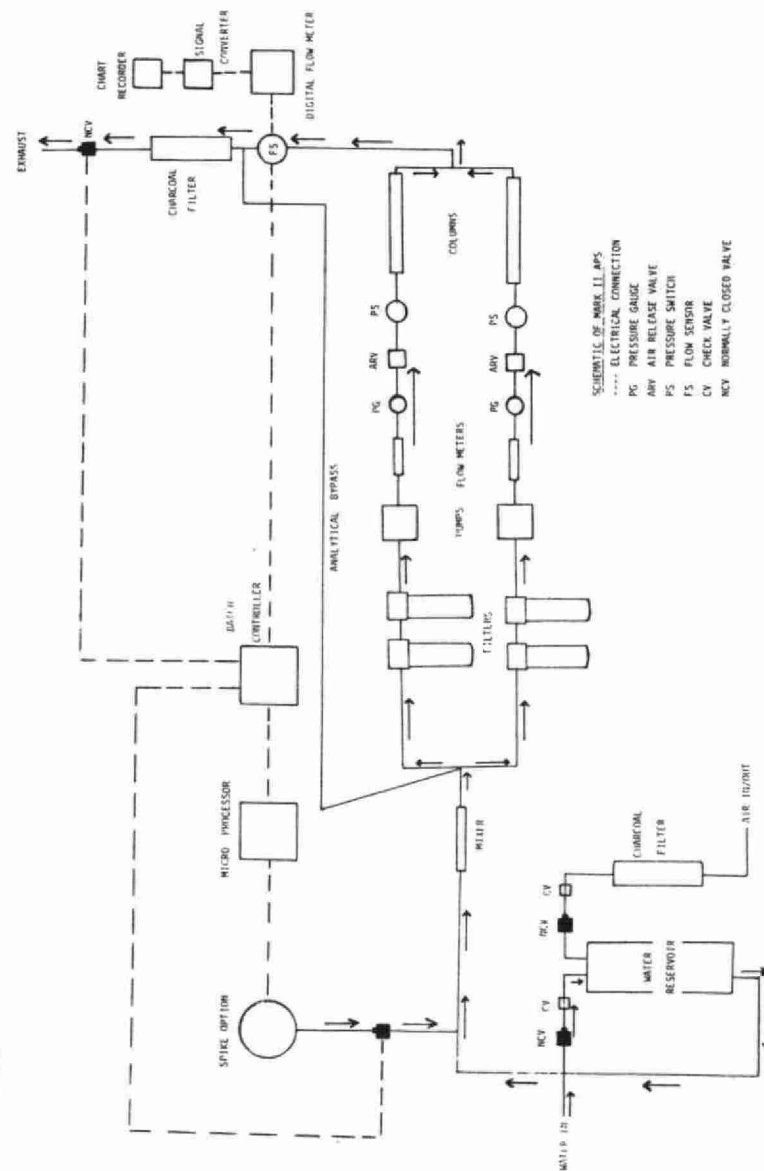
FIGURE 1

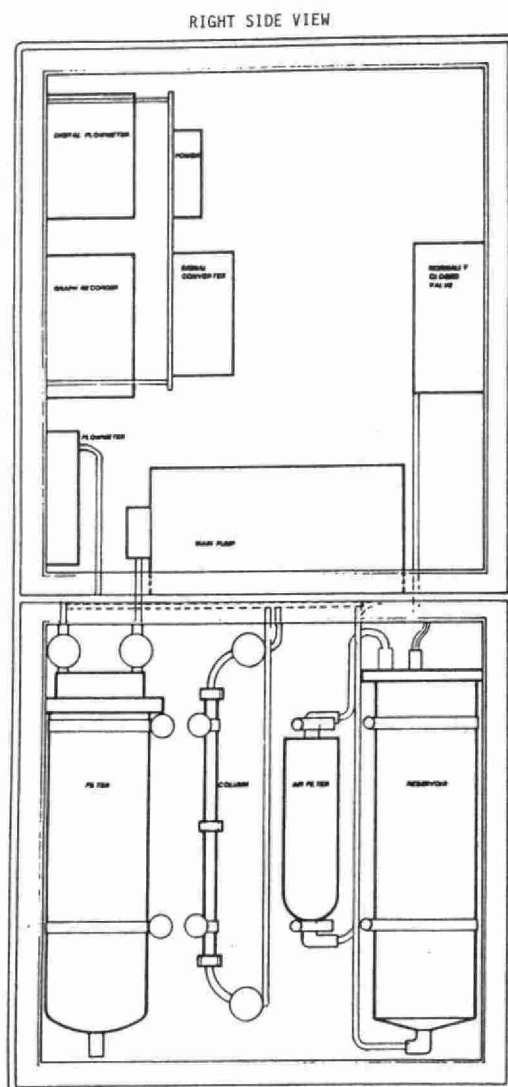SCHEMATIC OF MARK II APS
- - - - ELECTRICAL CONNECTION
PG   PRESSURE GAUGE
ARV   AIR RELEASE VALVE
PS   PRESSURE SWITCH
FS   FLOW SENSOR
CV   CHECK VALVE
NCV   NORMALLY CLOSED VALVE

RIGHT SIDE VIEW

FIGURE 2

FIGURE 3

LEFT SIDE VIEW

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